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A promising potential embeddable sensor for corrosion monitoring application in concrete structures

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Abstract

Sensors are involved in the corrosion monitoring and structural monitoring of concrete structures. In this investigation attempts have been made on the corrosion monitoring of concrete structures by employing embeddable reference sensor. Alkaline manganese dioxide (MnO_2) sensor was fabricated in the laboratory as suitable as an embeddable use into the concrete structures. The electrochemical stability of sensor in concrete environments was examined in saturated calcium hydroxide solutions, a synthetic concrete pore solution and an extracts obtained from ordinary Portland cement. Sensor is embedded into the concretes and the performance was studied in the absence and presence of chloride ions for the exposure period of 18 months. Polarisation behaviour and impedance characteristics of the sensor in mortar were carried out in three aqueous solutions namely distilled water, 3% NaCl solution and natural sea water. This investigation covers the tests in solutions representing concrete environments, electrochemical studies in mortar and the long-term exposure studies in concrete.

Keywords: Potential sensor; Corrosion monitoring; Reinforced concrete; Long-term tests

1. Introduction

Monitoring and control of corrosion of reinforcing steel in concrete requires reliable measurement of stable potentials. Embeddable reference electrodes are very useful in corrosion monitoring of concrete structures for long-term monitoring and potentiostatically controlled cathodic protection of reinforcement in concrete. Their use in laboratory work and field exposure tests is advisable for the purpose of ensuring valid exchange of data between laboratory and field work. The increasing use of remote monitoring also requires that reference electrodes be capable of delivering reliable stable performance over an extended period of time. Ideally, an embedded electrode should be placed as close to the steel surface. A perfect embeddable electrode must be stable, invariant to chemical and thermal

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changes in concrete, tolerant to climatic conditions and have ability to pass small currents with a minimum of polarization and hysteresis effects, display long term performance, be cost effective and result from an environmentally safe manufacturing process. McCarter and Øystein Vennesland recently published a detailed review on sensor systems for use in reinforced concrete structures [1]. A number of sensor systems allow monitoring of the electrical properties of the concrete and/or steel at discrete distances from the exposed surface. For example Schiebl's ladder represents a macrocell sensor which measures the macrocell current flow between each anode and cathode [2]. In order to study the water, ionic and moisture movement within the surface zone multi-ring electrode moisture sensor [3] and concrete sensor developed by McCarter et al. [4–7] were reported. The sensor system developed by McCarter et al. in a laboratory study is used to obtain the spatial distribution of electrical conductivity within the cover-zone of concrete specimens subjected to a range of natural exposure conditions. The testing methodology enables in-situ monitoring of the electrical conductivity and technical issues relating to site measurements are discussed [8]. The work also highlights the need for continual monitoring of the concrete as the electrical conductivity changes with time, depth and environment.

Chloride induced corrosion is widely recognized as a major reason for the loss of durability in reinforced concrete structures [9]. Basheer and Long attempted to use the principle of the ion migration test and developed chloride ion PERMIT migration tester [10,11].

Optical fiber sensor for measurement of stress in concrete structures [12] and galvanic sensor system for detecting the corrosion damage of the steel embedded in concrete structures were reported [13,14].

Reference electrodes for use with reinforced concrete structures were reported by several authors [15–17]. Recently Ha et al. reviewed the role of sensors in corrosion monitoring and durability assessment in concrete structures [18]. Manganese dioxide was tried as pH and humidity sensor [19–21]. The objective of this investigation is to study the performance characteristics of manganese dioxide as possible embeddable sensor for concrete in the presence and absence of chloride. The electrochemical stability of this sensor was tested in representative concrete environments namely saturated calcium hydroxide solution, synthetic concrete pore solutions and extracts derived from ordinary Portland cement. Sensors were embedded in mortar and concrete and their performance was monitored for the exposure period of 18 months. This study fulfills the evaluation of MnO_2 sensor in solution representing concrete environments, electrochemical characteristics in mortar and the long-term exposure tests in concrete.

2. Experimental

2.1. Embeddable sensor

Alkaline manganese dioxide (MnO_2) sensor was fabricated as per the procedure reported in our earlier publication [18] and briefly given as follows. MnO_2 electrode consists of three compartments namely a porous hydrated cement paste as bottom layer, a conductive alkaline slurry as middle layer and a powdered MnO_2 as top layer. The schematic of the embeddable type MnO_2 reference sensor is shown in Fig. 1 and the photograph is given in Fig. 2.

2.2. Materials

The ordinary Portland cement (OPC) conforming to KS:L 5201-1989 was used and the

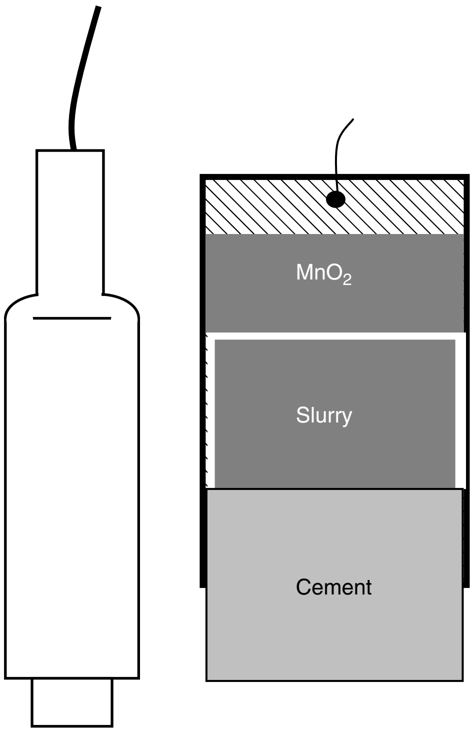

Fig. 1. A structure of MnO_2 electrode.

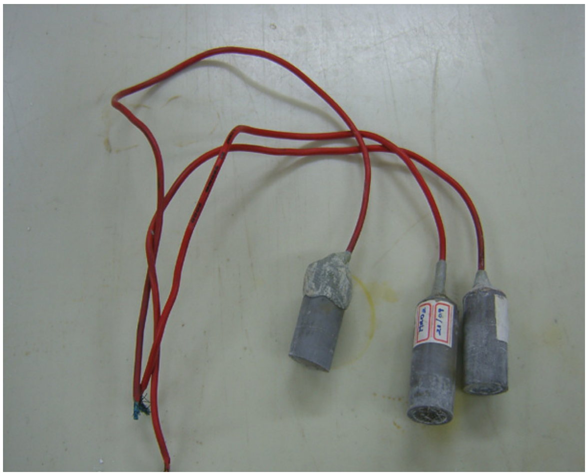

Fig. 2. Photograph for MnO_2 sensor.

composition was (wt%) CaO 63.8, SiO_2 21.8, Al_2O_3 5.1, Fe_2O_3 3.0, MgO 1.7, SO_3 2.0, LOI 0.8 and others 0.1. Fine and coarse aggregates are conforming to KS:F 2526:2002 was used. The fine and coarse aggregates are washed in distilled water and dried. Natural sea water collected from sea in Jin-Hae, South Korea was used.

2.3. Solutions

Saturated CaO solution was used. AR grade CaO was ignited for a long time to remove any carbonate present in the sample. Synthetic concrete pore solutions consists of 7.4 g NaOH and 36.6 g KOH per liter of saturated CaO. OPC extracts was prepared by using 100 gm of the OPC was dissolved in 200 ml of distilled water and then shaken mechanically for 1 h. Double distilled water obtained from Millipore was used for preparing all the solutions.

The pH of the solutions was measured using a standard portable ISTEK pH meter (Model 76P) with a relative accuracy of ±0.001. The pH of the solutions is 12.5, 13.5 and 13.0, respectively for saturated calcium hydroxide solution, a synthetic concrete pore solution and cement extracts.

2.4. Methods

2.4.1. Uniformity of fabricated sensors

The uniformity of potential of fabricated sensors was tested in the laboratory. The MnO_2 sensor is placed in a saturated solution of calcium hydroxide and the pH is maintained constant by the daily addition of CaO. The potentials are measured with respect to SCE. A salt bridge containing KNO_3 was used.

2.4.2. Stability tests in solutions

The electrochemical stability of the MnO_2 sensor was monitored in different test solutions representing concrete environments with respect to saturated calomel electrode (SCE) for the exposure period of 90 days. Experiments were also conducted simultaneously by a gradual addition of chloride. Addition of chloride is extended up to 30,000 ppm of NaCl into the test solutions.

2.4.3. Polarization behaviour of MnO_2 sensor embedded in concrete

Mortar (1:3 ratio cement: sand) specimen of size 6 cm diameter and 15 cm height were cast. The sensor electrode was embedded centrally on the mortars. All the mortars are subjected to curing in distilled water for 28 days in order to complete cement hydration reaction. Mortars are exposed to the natural weathering condition in the exposure yard for 18 months.

Potentiodynamic polarization was carried out in three aqueous solutions namely distilled water, 3% NaCl and natural sea water. Sensor embedded in mortar act as working electrode, perforated cylindrical stainless sheet act as counter electrode and SCE served as reference electrode. Polarization was carried out using Gamry Instruments, Inc at an ambient temperature of 25 ± 1 °C. Duplicate experiments were carried out for essentially to get same results.

2.4.4. Impedance characteristics of MnO_2 sensor embedded in concrete

Similar procedure was adopted for making mortar specimens for impedance studies. Impedance measurements were carried out using Solartron 1480 Multistat electrochemical measurement unit coupled with Solartron 1255-B Frequency Response Analyzer and multi media computer at an ambient temperature of 25 ± 1 °C. The real part (Z') and the imaginary part ($-Z''$) of the cell impedance were measured for various frequencies (100,000 to 0.01 Hz). Plots of Z' versus $-Z''$ were made. Duplicate experiments were carried out for essentially to get same results.

2.4.5. Long-term exposure tests in concrete

Cube concrete specimens of size 15 cm × 15 cm were cast using designed mix of M20 concrete. MnO_2 sensor was embedded centrally into the concrete. After 24 h, the concrete specimens were demoulded and cured for 28 days in distilled water. Specimens were cast with 0% and 3% chloride by weight of cement. All the concrete specimens were exposed to the natural weathering conditions at the exposure yard for 18 months. The half-cell potential of MnO_2 sensor was monitored periodically using the external saturated calomel electrode.

3. Results and discussion

3.1. Uniformity of MnO_2 reference electrode

Before delivery of any embeddable sensor electrodes, the potential of a particular sensor electrode is confirmed with well established saturated calomel electrode. Fig. 3 shows the results of the uniformity of MnO_2 reference electrode in saturated calcium hydroxide solution. For this experiment, 30 numbers of MnO_2 reference electrodes were made and tested in saturated calcium hydroxide solution. It was inferred that, out of 30 numbers of electrodes, 17 numbers are showed +175 mV, 8 numbers are +172 mV and 5 numbers are +170 mV vs. SCE. It is interesting to note that, not much variation was observed between these electrodes. The maximum variation observed was only ±5 mV vs. SCE and this difference in potential is almost negligible indicating that MnO_2 electrodes showed uniformity in concrete environments under laboratory condition.

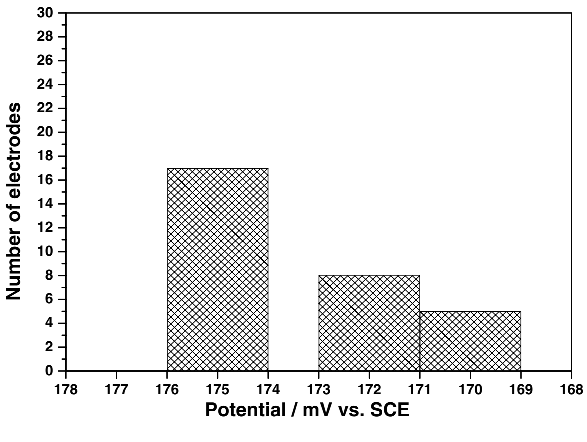

Fig. 3. Uniformity of measured potential of sensors in the saturated solution of calcium hydroxide.

3.2. Stability of MnO_2 sensor in concrete environments

The potential of MnO_2 electrode in concrete environments such as saturated calcium hydroxide solution, a synthetic concrete pore solution and in cement extracts are given in Table 1. The potential were measured for the exposure period of 90 days. It was observed from Table 1 that, the maximum and minimum measured potential values are +176 mV and +170 mV respectively in a synthetic concrete pore solution (pH 13.5). The difference of 6 mV alone was noticed in this solution. In the case of pH 12.5, the difference was found to be 6 mV. Cement extracts showed a difference of 5 mV only between maximum and minimum potential values. The stability in maintaining the potential for MnO_2 sensor in all the three test solutions representing concrete environments in the laboratory

Table 1
Potential values for MnO_2 sensor in concrete environments for the exposure period of 90 days

Days	Potential, mV vs. SCE		
	pH 13.5	pH 13.0	pH 12.5
1	170	165	170
3	175	167	172
9	175	168	173
12	177	168	174
15	175	165	173
18	175	163	172
21	174	162	171
24	173	163	169
27	174	162	170
30	175	165	171
33	176	161	172
36	175	162	169
39	175	164	171
42	174	165	171
45	173	165	171
48	173	166	170
51	174	162	169
54	175	168	171
57	175	166	170
60	173	165	172
63	175	167	172
66	173	166	172
69	177	166	171
72	175	167	172
75	174	168	173
78	174	165	170
81	175	166	171
84	176	165	173
87	176	166	172
90	176	166	173

condition are well within the range which reference sensors suitable for use in concrete structures in the field conditions.

Fig. 4. showed the behaviour of MnO_2 electrode in concrete environments with a different concentration of chloride. Here again the MnO_2 electrode proved that, a stable potential behaviour in all the chloride levels. This is quite suited for our interest to use of this MnO_2 electrode in the concrete structures in the presence of chloride ions.

3.3. Polarization behaviour of MnO_2 sensor embedded in mortar specimens

Ideally any reference sensor showed stable potential values. But if the sensor was used in the corrosion monitoring application, the stability may be altered due to its small application of current involved in the remote corrosion monitoring application of concrete structures. So an ideal sensor should not polarize to great extent even though they must be used in the field condition as an embeddable use. Any reference sensor able to withstand potential by applying small current during corrosion monitoring applications is considered as true reference sensors.

Polarization behaviour of MnO_2 sensor embedded in mortar was carried out in distilled water, 3% NaCl and natural sea water medium and the typical graphs are given in Fig. 5. It was observed from the figure that MnO_2 sensor embedded in mortar showed a very negligible current in the order of nA to μA in all the three aqueous solutions indicating that it able to stand small current with a minimum of polarization. Further, not much variation was noticed either in the cathodic or in the anodic polarization curves. In addition, a stable potential passive region was observed in the anodic direction. The presence of chloride also does not having any influence on the anodic direction. A good agreement in potential and current values was noticed in the case of 3% NaCl and natural sea water medium.

3.4. AC Impedance behaviour of MnO_2 sensors embedded in concrete

Nyquist plot were recorded for MnO_2 sensors embedded in mortar specimens in three aqueous solutions and are shown in Fig. 6. It was observed that only distorted semicircle was recorded for all the systems. The impedance diagram obtained in the distilled water medium was similar in shape and size to those in other solutions. The high frequency limit impedance value agreed well with the value expected from the test solution conductivities and mortar dimensions used. The high frequency arc did not vary greatly from solution to solution. The low frequency response was dominated by a constant phase angle element. No other admittance elements could be identified clearly at the low frequencies. The impedance behaviour of MnO_2 reference electrode embedded in mortar are found to be similar in all the three aqueous media studied.

The stability of MnO_2 electrode is due to the following reasons. The half-cell potential of MnO_2 is a complex function of the reduction state of manganese dioxide. But the potential being determined

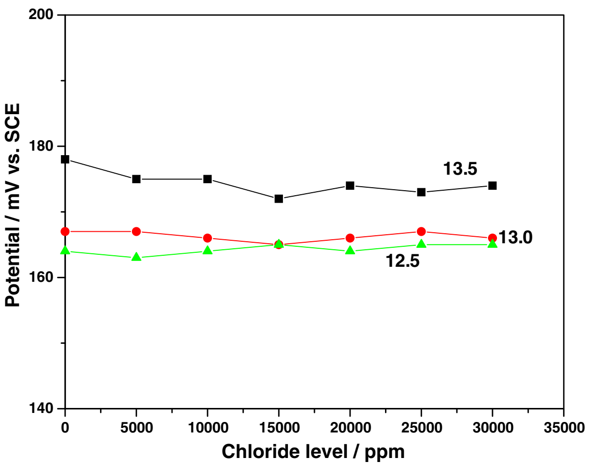

Fig. 4. Relation between potential and chloride level in concrete environments.

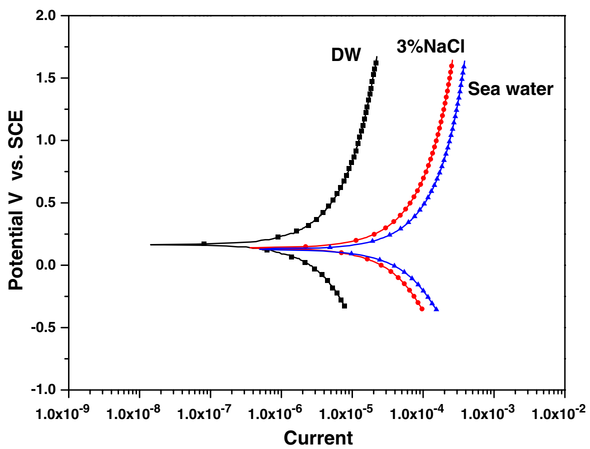

Fig. 5. Potentiodynamic scan of MnO_2 sensor embedded in mortar in distilled water (DW), 3% NaCl and natural sea water.

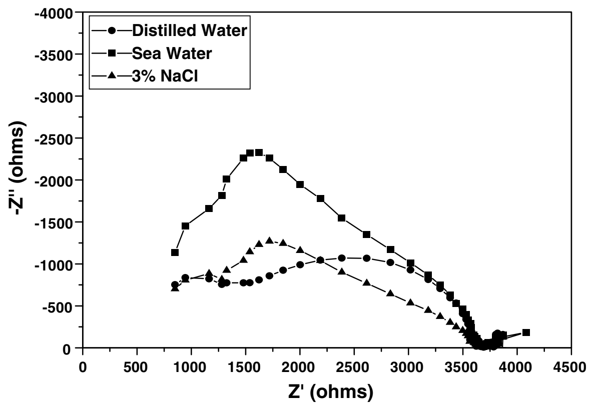

Fig. 6. Impedance behaviour of MnO_2 sensor embedded in mortar in distilled water, 3% NaCl and natural sea water.

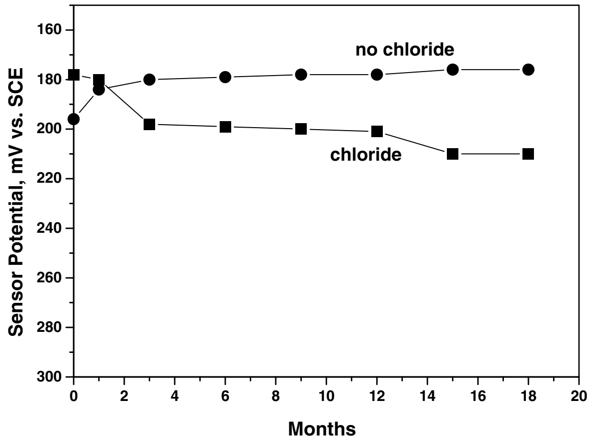

Fig. 7. Electrochemical stability of MnO_2 sensor embedded in concrete for the exposure period of 18 months.

by MnO_2/Mn_2O_3 equilibrium potential. In MnO_2 electrodes, the middle layer is slurry of pH of 13.5 corresponding to the pH of normal pore water and will take care of the chemical balance with the surrounding concrete. This is the most advantageous of the manganese dioxide electrode which is chloride free when compared to the well known Ag/AgCl electrode which is always surrounded by with chloride. The electrolytic contact of MnO_2 to the concrete environments is through the bottom layer which is made up of diffusion barrier of cement paste gives a good protection to the electrode unlike other electrodes. This will sufficiently give a good bond to the concrete and also means that the all important interface between the electrode and to the concrete environments. The liquid junction potential across this interface is very minimal because of the pH is nearly the same in the bottom plug and in the cell interior. This will expected not to develop any junction potential at the plug/concrete interface, if this sensory electrode is used in the field. The additional advantage of embeddable type MnO_2 is free from harmful elements like mercury or corrosion accelerators like chloride and sulphate. The superior performance of MnO_2 trigger the possibility of reliable embeddable type electrodes for the corrosion monitoring of concrete structures. MnO_2 is also considered as a true reference electrode for concrete.

3.5. Long-term exposure studies on the stability of MnO_2 sensors embedded in concrete

Long-term exposure studies on the MnO_2 sensor embedded in concrete specimens was carried out for 18 months out-side exposure under natural weathering conditions. The stability of potential was monitored periodically and are given in Fig. 7.

It was observed from Fig. 7 that, the potential of MnO_2 reference electrode showed constant for the exposure period 18 months. The potential-time behaviour for the chloride contaminated concrete is also shown in Fig. 7. The addition of chloride does not make any influence for the 18 months exposure period. The concrete specimens were split open and carefully removed the MnO_2 sensor and tested their integrity in the laboratory. In this case, the sensors taken from the outside exposure studies are placed in the saturated solution of calcium hydroxide and the potentials are measured with respect to SCE at 25 ± 1 °C. All the electrodes are able to show the stable potential of 176 ± 6 mV with respect to SCE indicating that the long-term performance of the MnO_2 sensor was good.

4. Conclusions

MnO_2 sensor seems to be the more stable and reliable potential sensor electrode in concrete medium and also in concrete structures. The uniformity of potential of MnO_2 sensor is reproducible and easy to test in the laboratory with respect to well known SCE electrode. The electrochemical characteristics of MnO_2 sensor embedded in mortar in three aqueous solutions showed a negligible polarization current and stable passive region. The long term stability in concrete under outside exposure studies also proved the better performance of MnO_2 sensor and possible use as an embeddable use in concrete structures for corrosion monitoring applications. Unlike conventional reference sensors, MnO_2 sensor is free from harmful elements like mercury and corrosion accelerators like sulphate and chloride. Advantageously MnO_2 sensor was able to use an embeddable type into new and old structures.

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